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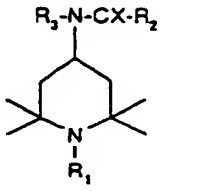
(54) Stabilizer combinations for halogen-containing polymers

(57) A stabilizer combination for halogen-containing polymers is described, comprising

A) at least one organozinc compound with a Zn-O bond and/or a Zn-S bond

B) at least one compound of the formula



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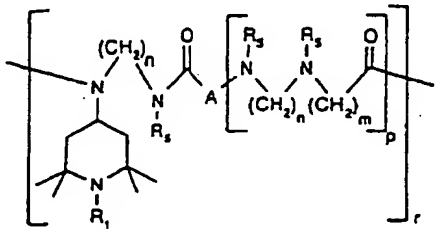

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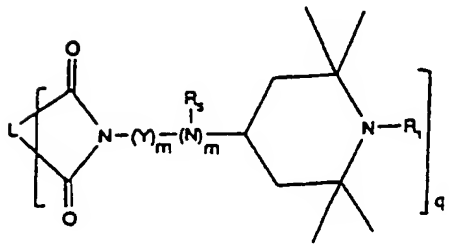

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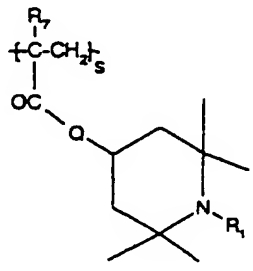

(IV)

in which R_1, R_2, R_3, R_5, R_7, A, m, n, p, q, r, s, L, Q, Y and X are as defined in claim 1.

At least some of the organozinc compound A) may be replaced by an inorganic zinc compound.

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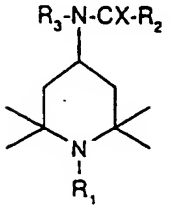
4-Acylamido-piperidine compounds in stabilizer combinations for chlorine-containing polymers

The invention relates to a stabilizer combination comprising an organozinc compound with an Zn-O and/or Zn-S bond, in particular a zinc carboxylate, and at least one compound of the formulae I, II, III and IV depicted below, which is suitable for stabilizing chlorine-containing polymers, especially PVC.

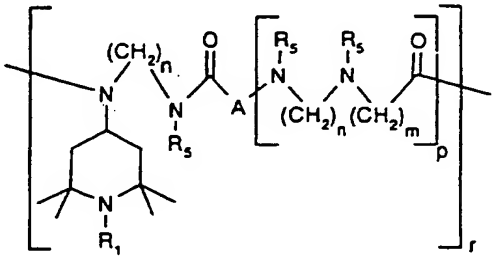
PVC can be stabilized by a range of additives. Compounds of lead, of barium and of cadmium are particularly suitable for this purpose, but are nowadays controversial on ecological grounds (cf. "Taschenbuch der Kunststoffadditive", Eds. R. Gächter and H. Müller, Carl Hanser Verlag, 3rd Edition, 1989, pages 303-311, and Kunststoff Handbuch PVC, Volume 2/1, G.W.Becker, D.Braun, Carl Hanser Verlag 1985, pages 531-538). The search is therefore continuing for effective stabilizers and stabilizer combinations devoid of disadvantageous properties.

Sterically hindered amines have already been added to the PVC as light stabilizers. The thermal stability may also be favourably affected (cf. e.g. EP-A-366271 and EP-A-488951).

It has now been found that organozinc compounds, such as zinc carboxylates, can be combined advantageously with compounds of the formulae



(I),



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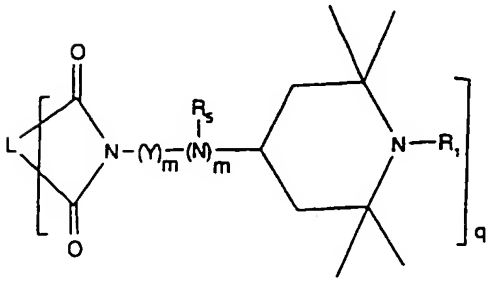

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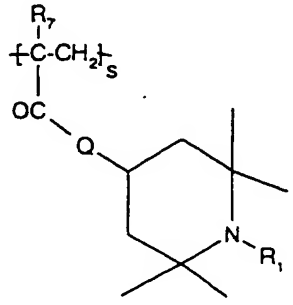


(IV)

in order to stabilize chlorine-containing polymers. In these formulae, the meanings of the radicals and symbols are as follows:

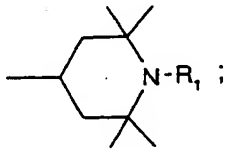
X: O or S;

a: 0 to 8; b: 2 to 12; c: 1 or 2; k: 2 to 6;

R_1 : H or C_1-C_8alkyl, C_3-C_8alkenyl, C_7-C_9phenylalkyl or C_5-C_8cycloalkyl;

R_2 : C_1-C_8alkyl, $-NH_2$, R_3NG-, R_4-O-, $[R_3$-NG-CX$]_c$E-,

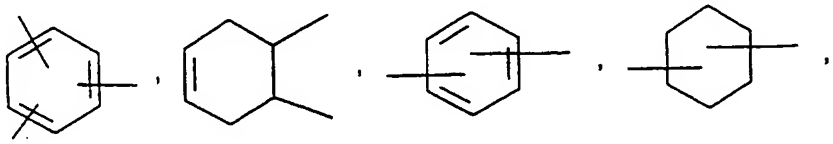
$(C_1$-C_4alkyl$)_2N(CH_2)_k$-CX-, phenyl or OH-, C_1-C_4alkoxy- or C_1-C_4alkyl-substituted phenyl,

G:  ;

R_3 : H, C_1-C_8alkyl, C_3-C_8alkenyl, C_5-C_8cycloalkyl, R_2-CX-NG-$(CH_2)_b$,

$(C_1$-C_4alkyl$)_2N(CH_2)_k$- or G;

R_4 : C1-C4alkyl, cyclohexyl or benzyl;

E: $(CH_2)_a$,  ,

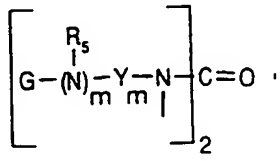
-CH=CH-, -CH(OH)-CH(OH)-, $-CH_2$-CH(OH)- or -NH $(CH_2)_b$NH-;

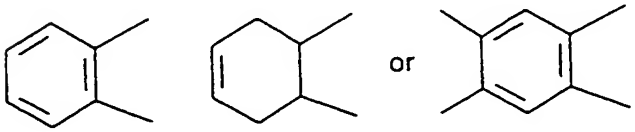
A: $-(CH_2)-_m$, >CO, $-(CH_2)_d$-CO- or $-NH(CH_2)_n$-CO-;

m: 0 or 1; n: 2 to 12; p: 0 or 1; d: 1 to 8; q: 1 or 2; r: 2 to 50;

and, if p is 0, A: >CO, $-(CH_2)-_m$, $-(CH_2)_d$-CO-, $-NH(CH_2)_n$-CO-;

if p is 1, A: $-(CH_2)$-m;

the group L: $-CH_2-CHR_6-$, $-(CH_2)-_3$, -CH=CH-,  ,

 ;

R_5 : H, C_1-C_8alkyl, C_3-C_8alkenyl, C_5-C_8cycloalkyl or G;

R_6 :H, C_1-C_{12}alkyl;

R_7 : H or CH_3;

Q: -O- or >NH;

Y : $-CH_2-CH(OH)-CH_2-$;

and s: 3 to 60.

In the above formulae:

C_1-C_4alkyl is methyl, ethyl, n-propyl, isopropyl, n-, i-, sec- or t-butyl.

C_1-C_8alkyl are the same radicals and, for example, n-pentyl, isopentyl, neopentyl, n-hexyl, n-heptyl, 2-ethylhexyl, n-octyl or isooctyl.

C_5-C_8cycloalkyl is, for example, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl. Cyclopentyl and, in particular, cyclohexyl are preferred.

C_3-C_8alkenyl substituents can be branched or unbranched alkenyl, for example allyl, crotonyl, 2-methylallyl or hexenyl.

C_1-C_4alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy or isobutoxy.

C_7-C_9phenylalkyl is, for example, benzyl, 1- or 2-phenylethyl, 3-phenylpropyl, alpha,alpha-dimethylbenzyl or 2-phenylisopropyl, preferably benzyl.

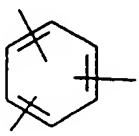
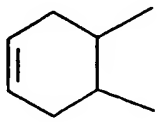
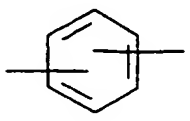
Preference is given in the stabilizer combination to compounds of the formulae I to IV, in which

X: O or S; a: 0 to 4; b: 2 to 6; c: 1 or 2; k: 2 or 3;

R^1 : H or C_1-C_8alkyl;

R_2 : C_1-C_8alkyl, $-NH_2$, R_3-NG-, $[R_3\text{-NG-CX}]_cE$- or $(C_1\text{-}C_4\text{alkyl})_2N(CH_2)_k$-CX-;

R_3 : H, C_1-C_8alkyl, R_2-CX-NG-$(CH_2)_b$, $(C_1\text{-}C_4\text{alkyl})_2N(CH_2)_k$- or -G;

E: $-(CH_2)^a$-,    -CH=CH- or

$-NH(CH_2)_bNH$-;

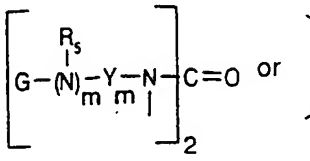
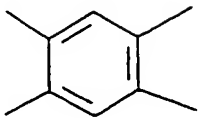
R_5 : H, C_1-C_8alkyl or G;

A: -CO-, $-(CH_2)_m$- , $-(CH_2)_d$-CO- or $-NH(CH_2)_n$-CO-;

m: 0 or 1; n: 2 to 6; p: 0 or 1; d: 1 to 4; q: 1 or 2; r: 2 to 50;

and, if p is 0, A: -CO-, $-(CH_2)_m-$, $-(CH_2)_d$-CO- or $-NH(CH_2)_n$-CO-;

if p is 1, A: $-(CH_2)_m-$;

the group L: $-CH_2-CHR_6-$, $-(CH_2)_3-$,  or  ;

R_6 : H or C_1-C_{12}alkyl;

Y: $-CH_2-CH(OH)-CH_2-$;

R_7 : H or CH_3;

Q: -O- or >NH,

and s: 3 to 60.

Particularly preferred compounds of the formulae I to IV are those in which

X: O;

a: 0 to 4; b: 2 to 6; c: 1;

R_1 : H or C_1-C_8alkyl;

R_2 : $[R_3$-NG-CX$]_c$E-;

R_3: H, C_1-C_8alkyl, R_2-CX-NG-$(CH_2)_b$ or G;

E: $(CH_2)_a$ or $-NH-(CH_2)_b-NH-$;

R_5 : G;

A : $-(CH_2)_m-$;

m: 0 or 1; n: 2 to 6; p: 0 ; q: 1 or 2; r: 2 to 50;

the group L: $-CH_2-CHR_6-$, $-(CH_2)_3-$, or -CH=CH-;

R_6 : H;

Y : $-CH_2-CH(OH)-CH_2-$;

R_7 : H ;

Q: >NH;

and s: 3 to 60.

Examples of the piperidine compounds of the formulae I to IV are:

01) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)ethylene-1,2-diacetamide

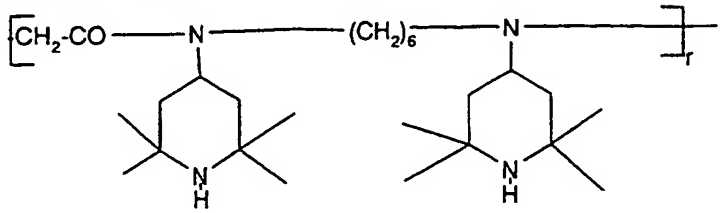
02) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)ethylene-1,2-formamide

03) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)adipamide

04) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)oxamide

05) 4-hydroxybenzamido-2,2,6,6-tetramethylpiperidine

06)



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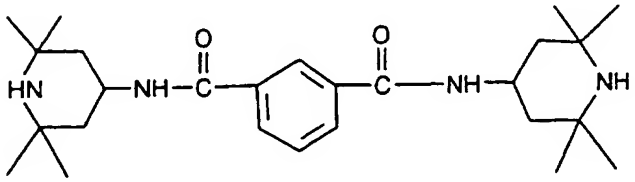

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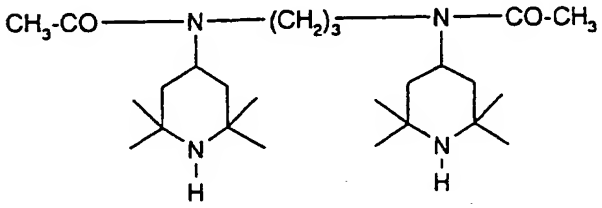

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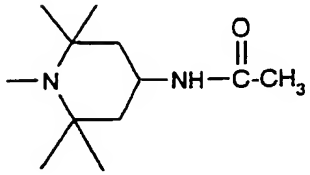

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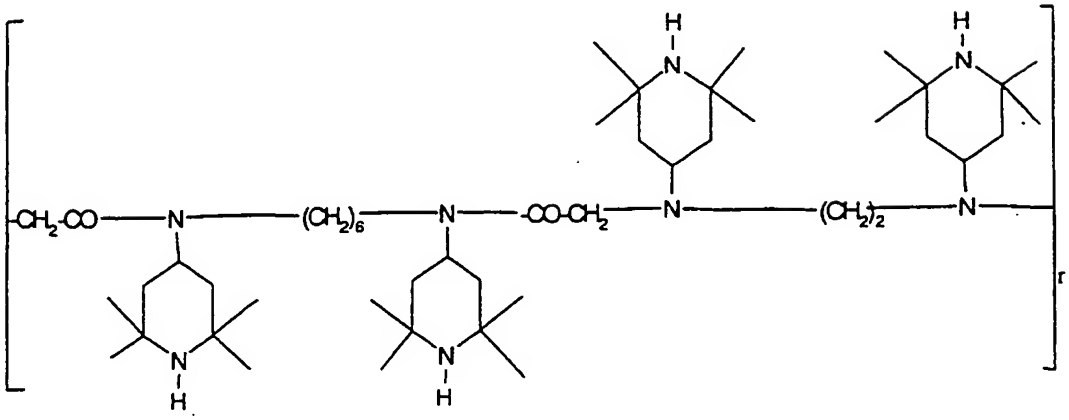
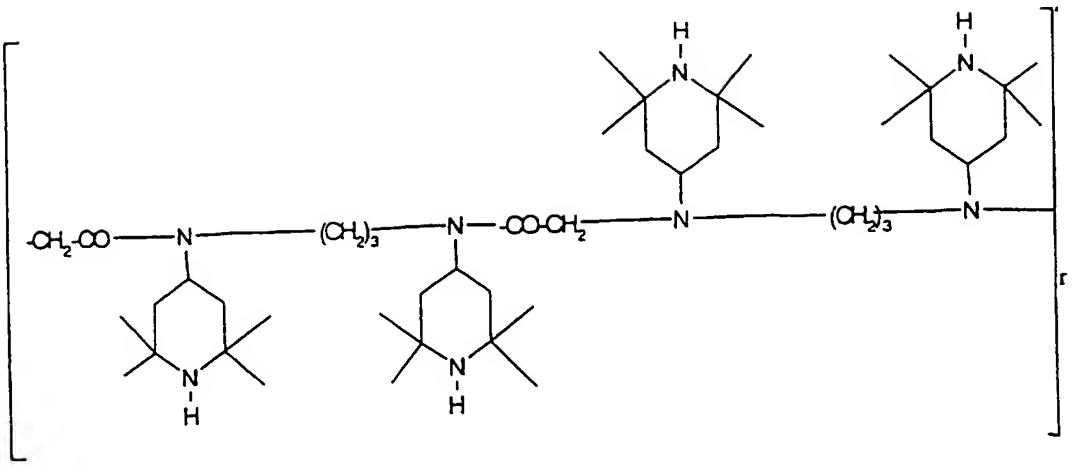
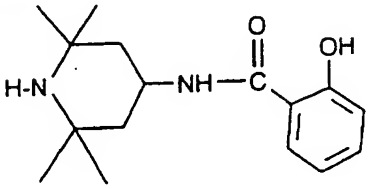
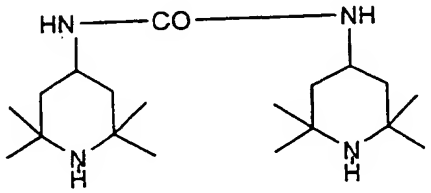
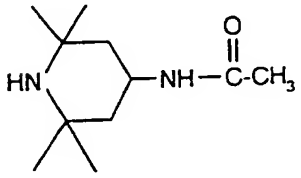
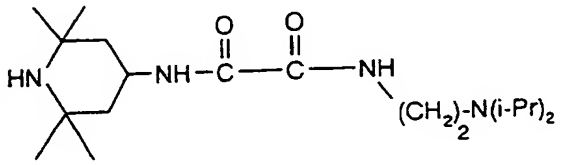


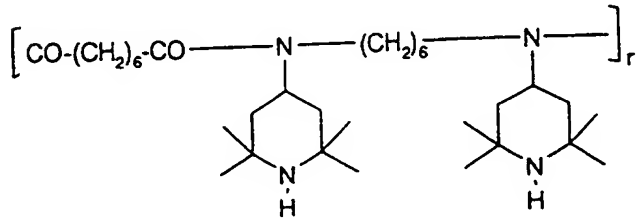
11) 

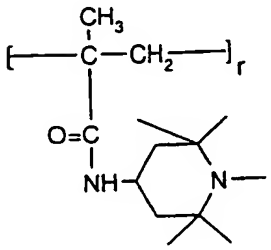
12) 

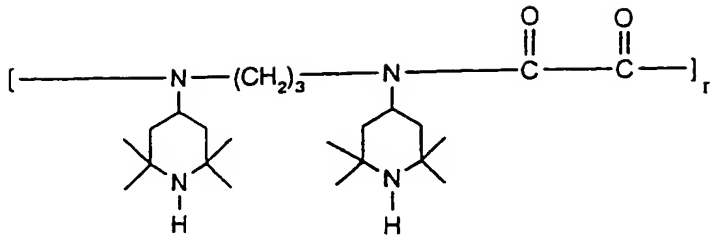
13) 

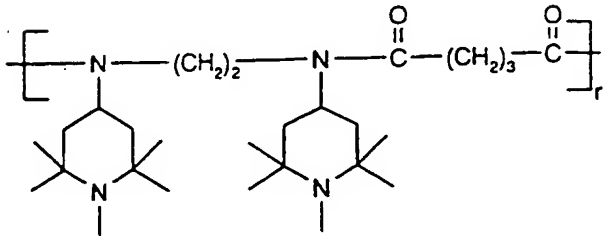
14) 

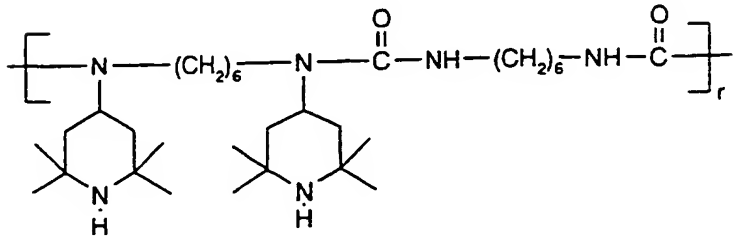
15) 

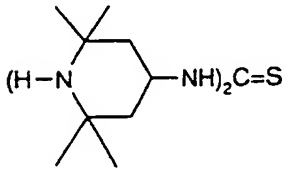
16) 

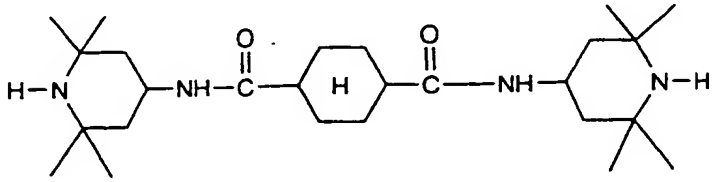
17) 

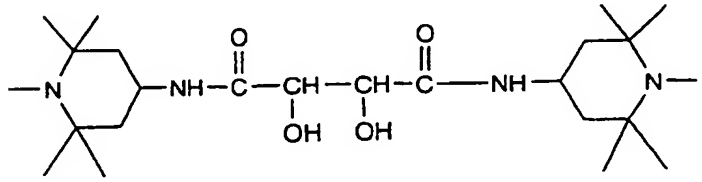
18) 

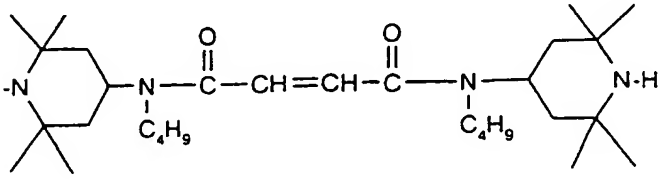
19) 

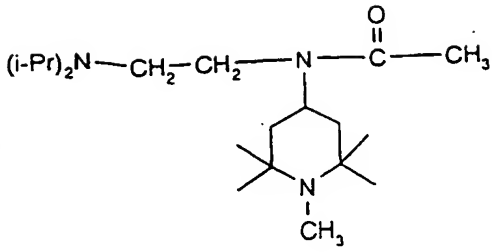
20) 

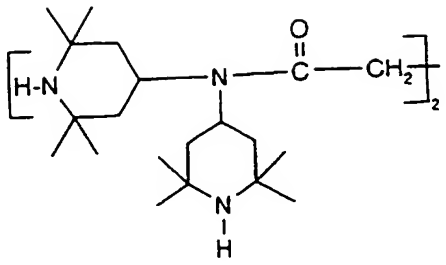
21) 

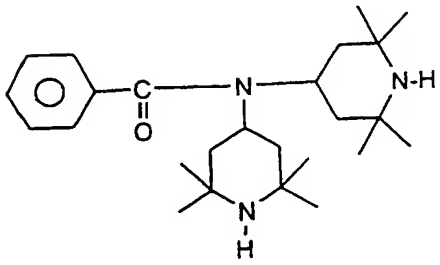
22) 

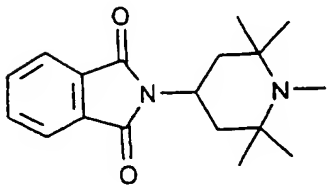
23) 

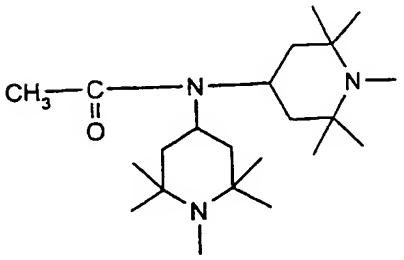
24) 

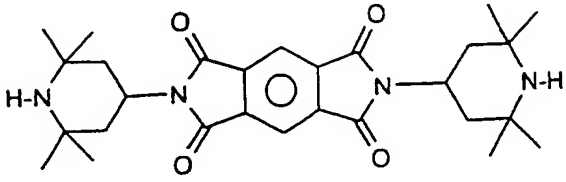
25) 

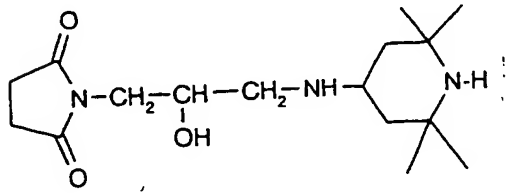
26) 

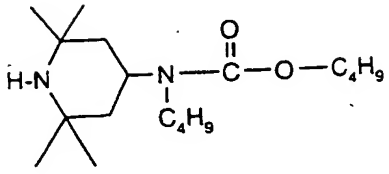
27) 

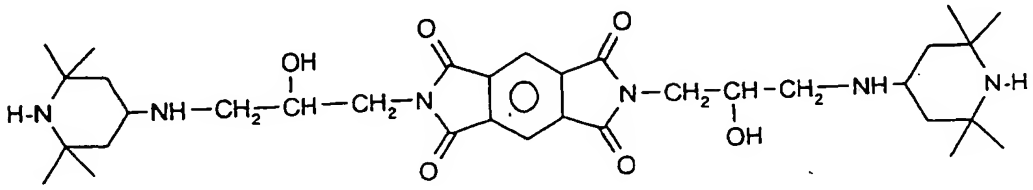
28) 

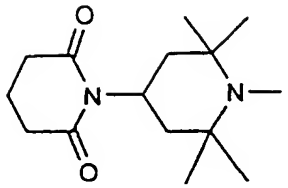
29) 

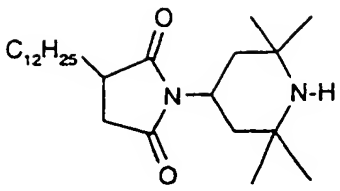
30) 

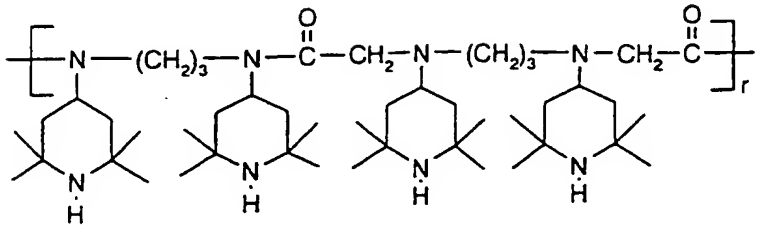
31) 

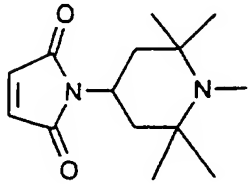
32) 

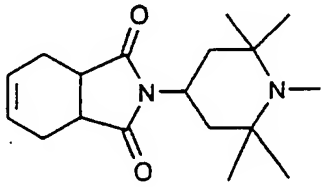
33) 

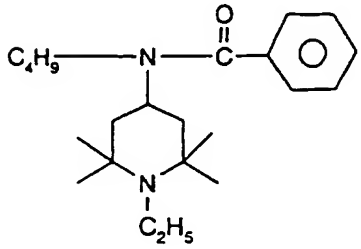
34) 

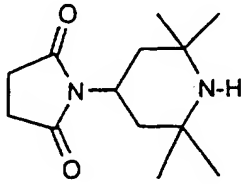
35) 

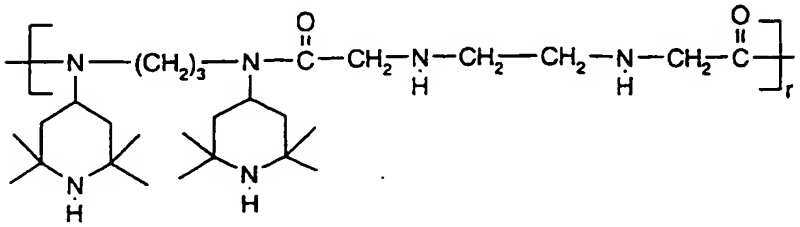
36) 

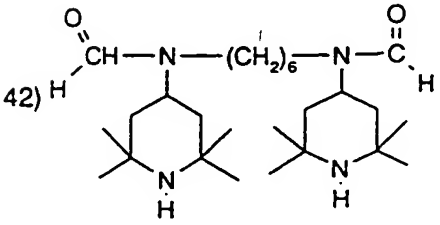
37) 

38) 

39) 

40) 

41) 

42) 

The compounds of the formulae I to IV can be present in the chlorine-containing polymer in proportions of from 0.005 to 5%, preferably from 0.01 to 2% and, in particular, from 0.01 to 1%.

Zinc compounds

The organozinc compounds with a Zn-O bond comprise zinc enolates, zinc phenolates and/or zinc carboxylates. The latter are compounds from the series of the aliphatic saturated and unsatured C_1-C_{22}carboxylates, the aliphatic saturated or unsaturated C_2-C_{22}carboxylates, which are substituted with at least one OH group or whose chain is interrupted by one or more O atoms (oxa acids), the cyclic and bicyclic carboxylates of 5-22 carbon atoms, the unsubstituted, mono- or poly-OH-substituted and/or C_{1-16}alkyl-substituted phenylcarboxylates, the phenyl-C_{1-16}alkylcarboxylates, or the unsubstituted or C_{1-12}alkyl-substituted phenolates, or of abietic acid. Examples of Zn-S compounds are Zn mercaptides, Zn mercaptocarboxylates and Zn mercaptocarboxylic esters.

Mention may be made by name, as examples, of the zinc salts of monovalent carboxylic acids, such as acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, oenanthic acid, octanoic acid, neodecanoic acid, 2-ethylhexanoic acid, pelargonic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, myristylic acid, palmitic acid, lauric acid, isostearic acid, stearic acid, 12-hydroxystearic acid, 9,10-dihydroxystearic acid, oleic acid, ricinoleic acid, 3,6-dioxaheptanoic acid, 3,6,9-trioxadecanoic acid, behenic acid, benzoic acid, p-tert-butylbenzoic acid, dimethylhydroxybenzoic acid, 3,5-di-tert-butyl-4-hydroxybenzoic acid, toluic acid, dimethylbenzoic acid, ethylbenzoic acid, n-propylbenzoic acid, salicylic acid, p-tert-octylsalicylic acid, and sorbic acid, cinnamic acid, mandelic acid, glycolic acid; zinc salts of divalent carboxylic acids and their monoesters, such as oxalic acid, malonic acid, succininic acid, glutaric acid, adipic acid, fumaric acid, pentane-1,5-dicarboxylic acid, hexane-1,6-dicarboxylic acid, heptane-1,7-dicarboxylic acid, octane-1,8-dicarboxylic acid, 3,6,9-trioxadecane-1,10-dicarboxylic acid, lactic acid, malonic acid, maleic acid, tartaric acid, malic acid, salicylic acid, polyglycoldicarboxylic acid (n=10-12), phthalic acid, isophthalic acid, terephthalic acid and hydroxyphthalic acid; and the di- or triesters of tri- or tetravalent carboxylic acids, such as hemimellitic acid, trimellitic acid, pyromellitic acid, citric acid and also so-called overbased zinc carboxylates, or zinc lauryl mercaptide, zinc thioglycolate, zinc thiosalicylate, zinc bis-i-octylthioglycolate, zinc mercaptopropionate, zinc thiolactate, zinc thiomalate, zinc bis-octylmercaptopropionate, zinc bis-isooctylthiolactate and zinc bis-laurylthiomalate.

The zinc enolates preferably comprise enolates of acetylacetone, of benzoylacetone, and of dibenzoylmethane and enolates of acetoacetic and benzoylacetic esters, and of

dehydroacetic acid. It is also possible to employ inorganic zinc compounds such as zinc oxide, zinc hydroxide, zinc carbonate, basic zinc carbonate or zinc sulfide.

Preference is given to neutral or basic zinc carboxylates of a carboxylic acid having 2 to 22 carbon atoms (zinc soaps), for example benzoates or alkanoates, preferably C_8alkanoates, stearate, oleate, laurate, palmitate, behenate, Versatate, hydroxystearates and -oleates, dihydroxystearates, p-tert-butylbenzoate, or (iso)octanoate. Particular preference is given to stearate, oleate, Versatate, benzoate, p-tert-butylbenzoate and 2-ethylhexanoate.

In addition to the abovementioned zinc compounds, (in)organic aluminium compounds having an Al-O bond are also suitable. The preferred aluminium compounds which can be used include, preferably, aluminium enolates and aluminium carboxylates. Examples of carboxylate and enolate radicals can be found correspondingly in the comments made regarding zinc above.

Examples of inorganic Al compounds are aluminium hydroxide and aluminium phosphates.

The described organozinc compounds and their mixtures can be employed in amounts of, for example, from 0.001 to 10 parts by weight, expediently from 0.01 to 5 parts by weight, preferably from 0.01 to 3 parts by weight, based on 100 parts by weight of chlorine-containing polymer.

They may also be present as mixed salts (coprecipitates).

The novel stabilizer combination can be used together with further additives which are customary for the processing and stabilization of chlorine-containing polymers, examples being

1. Stabilizers:

Epoxides and epoxidized fatty acid esters; phosphites; thiophosphites and thiophosphates; polyols; 1,3-dicarbonyl compounds; mercaptocarboxylic esters; dihydropyridines; antioxidants; light stabilizers and UV absorbers; alkali metal and alkaline earth metal compounds; perchlorate salts; zeolites; hydrotalcites; dawsonites;

2. Further common PVC additives, for example
lubricants; plasticizers; impact modifiers; processing aids; blowing agents; fillers; antistats; biocides; antifogging agents; pigments and dyes; metal deactivators; flameproofing agents (cf. in this respect "Handbook of PVC Formulating", E. J. Wickson, John Wiley & Sons, New York 1993).

Examples of such additives are known to the skilled worker and can be found in the technical literature. Without limitation, mention may be made here of some of the known additives and processing aids:

Phosphites: Organic phosphites are known co-stabilizers for chlorine-containing polymers. Examples are trioctyl, tridecyl, tridodecyl, tritridecyl, tripentadecyl, trioleyl, tristearyl, triphenyl, tricresyl, trisnonylphenyl, tris-2,4-t-butylphenyl or tricyclohexyl phosphite.

Further suitable phosphites are variously mixed aryl dialkyl and alky diarylphosphites, such as phenyl dioctyl, phenyl didecyl, phenyl didodecyl, phenyl ditridecyl, phenylditetradecyl, phenyl dipentadecyl, octyl diphenyl, decyl diphenyl, undecyl diphenyl, dodecyldiphenyl, tridecyl diphenyl, tetradecyl diphenyl, pentadecyl diphenyl, oleyl diphenyl, stearyl diphenyl and dodecyl bis-2,4-di-t-butylphenyl phosphite.

Furthermore, phosphites of various diols and polyols can also be used advantageously; examples are tetraphenyldipropylene glycol diphosphite, polydipropylene glycol phenyl phosphite, tetramethylolcyclohexanol decyl diphosphite, tetramethylolcyclohexanol butoxyethoxyethyl diphosphite, tetramethylolcyclohexanol nonylphenyl diphosphite, bisnonylphenyl di-trimethylolpropane diphosphite, bis-2-butoxyethyl di-trimethylolpropane diphosphite, trishydroxyethyl isocyanurate hexadecyl triphosphite, didecylpentaerythritol diphosphite, distearyl pentaerythritol diphosphite, bis-2,4-di-t-butylphenyl pentaerythritol diphosphite, and also mixtures of these phospites and aryl/alkyl phosphite mixtures of the statistical composition $(H_{19}C_9\text{-}C_6H_4)O_{1.5}P\ (OC_{12,13}H_{25,27})_{1.5}$ or $[C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}]_2P[i\text{-}C_8H_{17}O]$ or $(H_{19}C_9\text{-}C_6H_4)O_{1.5}P\ (OC_{9,11}H_{19,23})_{1.5}$.

The organic phosphites can be employed in an amount of, for example, from 0.01 to 10 parts by weight, expediently from 0.05 to 5 parts by weight and, in particular, from 0.1 to 3 parts by weight, based on 100 parts by weight of PVC.

Polyols: Examples of suitable compounds of this type are:
pentaerythritol, dipentaerythritol, tripentaerythritol, bistrimethylolpropane, trimethylolethane, bistrimethylolethane, trimethylolpropane, sorbitol, maltitol, isomaltitol, lactitol, lycasine, mannitol, lactose, leucrose, tris(hydroxyethyl) isocyanurate, palatinite, tetramethylolcyclohexanol (TMCH), tetramethylolcyclopentanol, tetramethylolcyclopyranol, glycerol, diglycerol, polyglycerol, thiodiglycerol, or 1-O-a-D-glycopyranosyl-D-mannitol

dihydrate, and also polyvinyl alcohol and cyclodextrins. Among these, TMCH and the disaccharide alcohols are preferred.

The polyols can be employed in an amount of, for example, from 0.01 to 20 parts by weight, expediently from 0.1 to 20 parts by weight, and, in particular, from 0.1 to 10 parts by weight, based on 100 parts by weight of PVC.

1,3-Dicarbonyl compounds: Examples of 1,3-dicarbonyl compounds are acetylacetone, butanoylacetone, heptanoylacetone, stearoylacetone, palmitoylacetone, lauroylacetone, 7-tert-nonylthioheptane-2,4-dione, benzoylacetone, dibenzoylmethane, lauroylbenzoylmethane, palmitoylbenzoylmethane, stearoylbenzoylmethane, isooctylbenzoylmethane, 5-hydroxycapronylbenzoylmethane, tribenzoylmethane, bis(4-methylbenzoyl)methane, benzoyl-p-chlorobenzoylmethane, bis(2-hydroxybenzoyl)methane, 4-methoxybenzoylbenzoylmethane, bis(4-methoxybenzoyl)methane, 1-benzoyl-1-acetylnonane, benzoylacetylphenylmethane, stearoyl-4-methoxybenzoylmethane, bis(4-tert-butylbenzoyl)methane, benzoylformylmethane, benzoylphenylacetylmethane, bis(cyclohexanoyl)methane, di(pivaloyl)methane, acetoacetic methyl, ethyl, hexyl, octyl, dodecyl or octadecyl ester, benzoylacetic ethyl, butyl, 2-ethylhexyl, dodecyl or octadecyl ester, stearoylacetic ethyl, propyl, butyl, hexyl or octyl ester and dehydroacetic acid, and the zinc, alkali metal, alkaline earth metal or aluminium salts thereof.

The 1,3-dicarbonyl compounds can be employed in an amount of, for example, from 0.01 to 10 parts by weight, expediently from 0.01 to 3 parts by weight and, in particular, from 0.01 to 2 parts by weight, based on 100 parts by weight of PVC.

Thiophosphites and thiophosphates: Thiophosphites and thiophosphates are compounds of the general type
$(RS)_3P$, $(RS)_3P=O$ and $(RS)_3P=S$, as described in the patent documents DE 2809492, EP 090770 and EP 573394. Examples are: trithiohexyl phosphite, trithiooctyl phosphite, trithiolauryl phosphite, trithiobenzyl phosphite, tris[carboxy-i-octyloxy]methyl trithiophosphate, S,S,S-tris[carbo-i-octyloxy]methyl trithiophosphate, S,S,S-tris[carbo-2-ethylhexyloxy]methyl trithiophosphate, S,S,S,-tris-1-[carbohexyloxy]ethyl trithiophosphate, S,S,S-tris-1-[carbo-2-ethylhexyloxy]ethyl trithiophosphate, S,S,S-tris-2-[carbo-2-ethylhexyloxy]ethy trithiophosphate.

The thiophosphites and thiophosphates can be present in the chlorine-containing polymer expediently in proportions of from 0.01 to 20%, preferably from 0.1 to 5% and, in particular, from 0.1 to 1%.

Mercaptocarboxylic esters: Examples of these compounds are: esters of thioglycolic acid, thiomalic acid, mercaptopropionic acids, of mercaptobenzoic acids and of thiolactic acid, as are described in FR 2459816, EP 90748, FR 2552440 and EP 365483. The mercaptocarboxylic esters also embrace corresponding polyol esters and their partial esters.

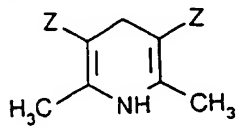
They can be present in the chlorine-containing polymer expediently in proportions of from 0.01 to 10%, preferably from 0.1 to 5% and, in particular, from 0.1 to 1%.

Epoxides and epoxidized fatty acid esters: The novel stabilizer combination may additionally comprise at least one epoxidized fatty acid ester. Particularly suitable for this are esters of fatty acids from natural sources, such as soya oil or rapeseed oil.

The epoxy compounds are employed in amounts of, for example, upwards of 0.1 part per 100 parts by weight of composition, expediently from 0.1 to 30 parts, preferably from 0.5 up to 25 parts by weight. Further examples are epoxidized polybutadiene, epoxidized linseed oil, epoxidized fish oil, epoxidized tallow, methylbutyl or 2-ethylhexyl epoxystearate, tris-(epoxypropyl)isocyanurate, epoxidized castor oil, epoxidized sunflower oil, 3-phenoxy-1,2-epoxypropane, bisphenol A diglycidyl ether, vinylcyclohexene diepoxide, dicyclopentadiene diepoxide and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate.

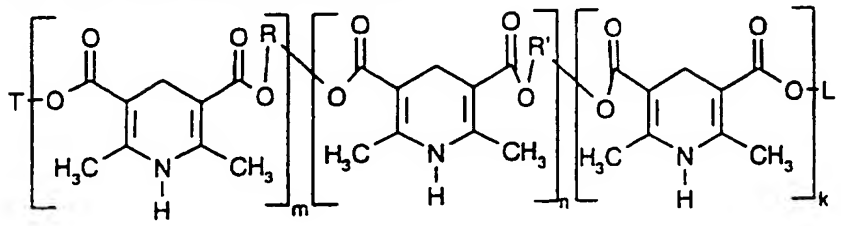
Also suitable as **epoxides** are derivatives of bisphenol A and of bisphenol F, as described, for example, in South African patent document ZA-2600/94.

Dihydropyridines and polydihydropyridines: Suitable monomeric dihydropyridines are compounds as described, for example, in FR 2039496, EP 2007, EP 362012 and EP 24754. Preference is given to those of the formula



in which Z is CO_2CH_3, $CO_2C_2H_5$, $CO_2{}^nC_{12}H_{25}$ or $-CO_2C_2H_4-S-{}^nC_{12}H_{25}$.

Particularly suitable polydihydropyridines are compounds of the following formula



in which T is unsubstituted C_{1-12}alkyl,

L is as defined for T,

m and n are numbers from 0 to 20,

k is 0 or 1,

R and R' independently of one another are ethylene, propylene, butylene or an alkylene- or cycloalkylenebismethylene group of the type $-(-C_pH_{2p}-X-)_tC_pH_{2p}-$,

p is from 2 to 8,

t is from 0 to 10, and

X is oxygen or sulfur.

Compounds of this kind are described in more detail in EP 0286887.

The (poly)dihydropyridines can be employed in the chlorine-containing polymer expediently in proportions of from 0.001 to 5 parts by weight and, in particular, from 0.005 to 1 part by weight, based on the polymer.

Particular preference is given to thiodiethylenebis[5-methoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine-3-carboxylate].

Alkali metal and alkaline earth metal compounds: By these terms are meant principally the carboxylates of the above-described acids, or also corresponding oxides and hydroxides, carbonates or basic carbonates. Also suitable are mixtures thereof with organic acids. Examples are NaOH, KOH, CaO, $Ca(OH_2)$, MgO, $Mg(OH)_2$, $CaCO_3$, $MgCO_3$, dolomite, huntite, and also Na, K, Ca or Mg salts of fatty acids.

In the case of carboxylates of alkaline earth metals and of Zn, it is also possible to employ adducts thereof with MO or $M(OH)_2$ (M = Ca, Mg, Sr or Zn), so-called overbased compounds.

Preference is given to the use, in addition to the novel stabilizer combination, of alkali metal, alkaline earth metal and/or aluminium carboxylates, for example Na, K, Ca or aluminium stearates.

Perchlorate salts: Examples are those of the formula $M(ClO_4)_n$ where M is Li, Na, K, Mg, Ca, Ba, Zn, Al, Ce or La. The index n is, in accordance with the valency of M, 1, 2 or 3. The perchlorate salts can be present as complexes with alcohols or ether alcohols. In this context, the respective perchlorate can be employed in various common forms in which it is supplied; for example as a salt or aqueous solution applied to a carrier material such as PVC, Ca silicate, zeolites or hydrotalcites, or obtained by chemical reaction of hydrotalcite with perchloric acid.

The perchlorates can be employed in an amount of, for example, from 0.001 to 5 parts by weight, expediently from 0.01 to 3 parts by weight and, with particular preference, from 0.01 to 2 parts by weight, based on 100 parts by weight of PVC.

Hydrotalcites and zeolites: The chemical composition of these compounds is known to the skilled worker, for example from the patent documents DE 3843581, US 4000100, EP 062813, WO 93/20135.

Compounds from the series of the hydrotalcites can be described by the general formula VI

$$M^{2+}_{1-x} \cdot M^{3+}_{x} \cdot (OH)_2 \cdot (A^{n-})_{x/n} \cdot mH_2O \qquad (VI)$$

in which

M^{2+} = one or more metals from the group consisting of Mg, Ca, Sr, Zn and Sn,

M^{3+} = Al or B,

A^n is an anion having the valency n,

n is a number from 1-2,

$0 < x \leq 0.5$, and

m is a number from 0-20.

A^n is preferably = OH^-, ClO_4^-, HCO_3^-, CH_3COO^-, $C_6H_5COO^-$, CO_3^{2-}, SO_4^{--}, HSO_4^-, $\begin{matrix}COO^-\\|\\COO^-\end{matrix}$,
$(CHOHCOO)_2^{2-}$, $(CH_2COO)_2^{2-}$, $CH_3CHOHCOO^-$, HPO_3^{2-} or HPO_4^{2-};

Examples of hydrotalcites are
$Al_2O_3.6MgO.CO_2.12H_2O$, $Mg_{4.5}Al_2(OH)_{13}.CO_3.3.5H_2O$, $4MgO.Al_2O_3.CO_2.9H_2O$,
$4MgO.Al_2O_3.CO_2.6H_2O$, $ZnO.3MgO.Al_2O_3.CO_2.8\text{-}9H_2O$ and $ZnO.3MgO.Al_2O_3.CO_2.5\text{-}6H_2O$.

Compounds from the series of the zeolites (alkali metal and/or alkaline earth metal aluminosilicates) can be described by the general formula (VII)

$$M_{x/n}[(AlO_2)_x (SiO_2)_y].wH_2O \quad (VII)$$

in which n is the charge of the cation M;
M is an element from the first or second main group, such as Li, Na, K, Mg, Ca, Sr or Ba, or Zn,
y:x is a number from 0.8 to 15, preferably from 0.8 to 1.2; and
w is a number from 0 to 300, preferably from 0.5 to 30.

Structures can be found, for example, in the "Atlas of Zeolite" by W.M. Meier and D.H. Olson, Butterworth-Heinemann, 3rd ed. 1992.

Examples of zeolites are sodium alumosilicates of the formulae $Na_{12}Al_{12}Si_{12}O_{48}$. 27 H_2O [zeolite A], $Na_6Al_6Si_6O_{24}$. 2 NaX . 7.5 H_2O, X= OH, halogen, ClO_4 [sodalite]; $Na_6Al_6Si_{30}O_{72}$. 24 H_2O; $Na_8Al_8Si_{40}O_{96}$. 24 H_2O; $Na_{16}Al_{16}Si_{24}O_{80}$. 16 H_2O; $Na_{16}Al_{16}Si_{32}O_{96}$. 16 H_2O; $Na_{56}Al_{56}Si_{136}O_{384}$. 250 H_2O [zeolite Y], $Na_{86}Al_{86}Si_{106}O_{384}$. 264 H_2O [zeolite X];

or the zeolites which can be prepared by partial or complete exchange of the Na atoms by Li, K, Mg, Ca, Sr or Zn atoms, such as
$(Na,K)_{10}$ $Al_{10}Si_{22}O_{64}$. 20 H_2O ; $Ca_{4.5}Na_3$ $[(AlO_2)_{12}$ $(SiO_2)_{12}]$. 30 H_2O; K_9Na_3 $[(AlO_2)_{12}$ $(SiO_2)_{12}]$. 27 H_2O.

Other suitable zeolites are:
$Na_2O \cdot Al_2O_3 \cdot$ (2 to 5) $SiO_2 \cdot$ (3.5 to 10) H_2O [zeolite P]
$Na_2O \cdot Al_2O_3 \cdot 2$ $SiO_2 \cdot$ (3.5-10)H_2O (zeolite MAP)
or the zeolites which can be prepared by partial or complete exchange of the Na atoms by Li, K or H atoms, such as
$(Li,Na,K,H)_{10}$ $Al_{10}Si_{22}O_{64}$. 20 H_2O, K_9Na_3 $[(AlO_2)_{12}$ $(SiO_2)_{12}]$. 27 H_2O, $K_4Al_4Si_4O_{16} \cdot 6H_2O$ [zeolite K-F], $Na_8Al_8Si_{40}O_{96}$.24 H_2O zeolite D, as described in Barrer et al., J. Chem. Soc. 1952, 1561-71, and in US 2,950,952;

Also suitable are the following zeolites:
K offretite, as described in EP-A-400,961; zeolite R, as described in GB 841,812; zeolite LZ-217, as described in US 4,503,023; Ca-free zeolite LZ-218, as described in US

4,333,859; zeolite T, zeolite LZ-220, as described in US 4,503,023; $Na_3K_6Al_9Si_{27}O_{72}.21\ H_2O$ [zeolite L]; zeolite LZ-211, as described in US 4,503,023; zeolite LZ-212 as described in US 4,503,023; zeolite O, zeolite LZ-217 as described in US 4,503,023; zeolite LZ-219, as described in US 4,503,023; zeolite rho, zeolite LZ-214, as described in US 4,503,023; zeolite ZK-19, as described in Am. Mineral. **54** 1607 (1969); zeolite W (K-M), as described in Barrer et al., J. Chem. Soc. **1956**, 2882; and $Na_{30}Al_{30}Si_{66}O_{192}.\ 98\ H_2O$ [zeolite ZK-5, zeolite Q].

Particular preference is given to the use of zeolite P types of the formula VII in which x is 2 to 5 and y is 3.5 to 10, especially zeolite MAP of the formula VII in which x is 2 and y is 3.5 to 10. The substance concerned is, in particular, zeolite Na-P, i.e. M is Na. This zeolite occurs generally in the variants Na-P-1, NaP-2 and Na-P-3, which differ in their cubic, tetragonal or orthorhombic structure (R.M.Barrer, B.M.Munday, J.Chem.Soc. A **1971**, 2909-14). The literature reference just mentioned also describes the preparation of zeolite P-1 and P-2. Zeolite P-3 is accordingly very rare and therefore of virtually no practical interest. The structure of zeolite P-1 corresponds to the gismondite structure known from the abovementioned Atlas of Zeolite Structures. In more recent literature (EP-A-384 070) a distinction is made between cubic (zeolite B or P_C) and tetragonal (zeolite P_1) zeolite of the P type. Also mentioned therein are more recent zeolites of the P type with Si:Al ratios below 1.07:1. These are zeolites bearing the designation MAP or MA-P, for Maximum Aluminium P. Depending on the preparation process, zeolite P may include small fractions of other zeolites. Highly pure zeolite P has been described in WO 94/26662.

In the context of the invention it is also possible to use those finely divided, water-insoluble sodium alumosilicates which have been precipitated in the presence of water-soluble inorganic or organic dispersants and crystallized. These can be introduced in the reaction mixture in any desired manner, prior to or during the precipitation or crystallization.

Preference is given to Na-zeolite A and Na-zeolite P.

The hydrotalcites and zeolites can be naturally occurring minerals or synthetically prepared compounds.

The hydrotalcites and/or zeolites can be employed in amounts of, for example from 0.1 to 50 parts by weight, expediently from 0.1 to 10 parts by weight and, in particular, from 0.1 to 5 parts by weight, based on 100 parts by weight of halogen-containing polymer.

Alkali metal alumocarbonates (dawsonites): These compounds can be represented by the formula

$\{(M_2O)_m.(Al_2O_3)_n Z_o.pH_2O\}$ (V) ,

in which M is H, Li, Na, K, $Mg_{1/2}$, $Ca_{1/2}$, $Sr_{1/2}$ or $Zn_{1/2}$; Z is CO_2, SO_2, $(Cl_2O_7)_{1/2}$, B_4O_6, S_2O_2 (thiosulfate) or C_2O_2 (oxalate); m, if M is $Mg_{1/2}$ or $Ca_{1/2}$, is a number between 1 and 2, in all other cases a number between 1 and 3; n is a number between 1 and 4; o is a number between 2 and 4; and p is a number between 0 and 30.

The alumo salt compounds of the formula (V) which can be used can be naturally occurring minerals or synthetically prepared compounds. The metals can be partially substituted by one another. The abovementioned alumo salt compounds are crystalline, partially crystalline or amorphous or can be present in the form of a dried gel. The alumo salt compounds can also be present in rarer, crystalline modifications. A process for preparing such compounds is specified in EP 394670. Examples of naturally occurring alumo salt compounds are indigirite, tunisite, alumohydrocalcite, para-alumohydrocalcite, strontiodresserite and hydro-strontiodresserite. Further examples of alumo salt compounds are potassium alumocarbonate $\{(K_2O).(Al_2O_3).(CO_2)_2.2H_2O\}$, sodium alumothiosulfate $\{(Na_2O).(Al_2O_3).(S_2O_2)_2.2H_2O\}$, potassium alumosulfite $\{(K_2O).(Al_2O_3).(SO_2)_2.2H_2O\}$, calcium alumooxalate $\{(CaO).(Al_2O_3).(C_2O_2)_2.5H_2O\}$, magnesium alumotetraborate $\{(MgO).(Al_2O_3).(B_4O_6)_2.5H_2O\}$, $\{([Mg_{0.2}Na_{0.6}]_2O).(Al_2O_3).(CO_2)_2.4.1H_2O\}$, $\{([Mg_{0.2}Na_{0.6}]_2O).(Al_2O_3).(CO_2)_2.4.3H_2O\}$ and $\{([Mg_{0.3}Na_{0.4}]_2O).(Al_2O_3).(CO_2)_{2.2}.4.9H_2O\}$.

The mixed alumo salt compounds can be obtained in accordance with methods known per se by cationic exchange, preferably from the alkali metal alumo salt compounds, or by combined precipitation (see for example US 5,055,284).

Preferred alumo salt compounds are those of the above formula in which M is Na or K; Z is CO_2, SO_2 or $(Cl_2O_7)_{1/2}$; m is 1-3; n is 1-4; o is 2-4 and p is 0-20. Z is particularly preferably CO_2.

Also preferred are compounds which can be represented by the following formulae:
$M_2O.Al_2O_3.(CO_2)_2 . pH_2O$ (Ia), $(M_2O)_2.(Al_2O_3)_2.(CO_2)_2 . pH_2O$ (Ib),
$M_2O.(Al_2O_3)_2.(CO_2)_2 . pH_2O$ (Ic)

in which M is a metal such as Na, K, $Mg_{1/2}$, $Ca_{1/2}$, $Sr_{1/2}$ or $Zn_{1/2}$ and p is a number from 0 to 12.

Particular preference is given to sodium alumodihydroxycarbonate (DASC) and the homologous potassium compound (DAPC).

The dawsonites can be employed in an amount of, for example, from 0.01 to 50 parts by weight, expediently from 0.1 to 10 parts by weight, particularly preferably from 0.1 to 5 parts by weight, based on 100 parts by weight of halogen-containing polymer.

The novel stabilizer combination can be used together with further additives which are customary for the processing and stabilizing of chlorine-containing polymers, examples being:
Antioxidants: Suitable examples are:

1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(a-methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyl tridec-1'-yl)phenol and mixtures thereof.

2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecyl-thiomethyl-4-nonylphenol.

3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

4. Tocopherols, for example a-tocopherol, b-tocopherol, g-tocopherol, d-tocopherol and mixtures thereof (vitamin E).

5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methyl-phenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis-(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide.

6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(a-methyl-cyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis-(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis-(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylene-bis[6-(a-methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(a,a-dimethylbenzyl)-4-nonyl-phenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methyl-phenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-di-hydroxydibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithio-terephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

8. Hydroxybenzylated malonates, for example dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, dioctadecyl 2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecyl mercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, di-[4-(1,1,3,3-tetramethylbutyl)phenyl] 2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

10. Triazine compounds, for example 2,4-bisoctylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate.

11. Benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzyl-phosphonate, diethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzyl-phosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzyl-phosphonic acid.

12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

13. Esters of b-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

14. Esters of b-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonane-diol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylol-propane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

15. Esters of b-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)-

oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

17. Amides of b-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, for example N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.
If desired it is also possible to employ a mixture of antioxidants differing in structure.

The antioxidants can be employed in an amount of, for example, from 0.01 to 10 parts by weight, expediently from 0.05 to 10 parts by weight and, in particular, from 0.05 to 5 parts by weight, based on 100 parts by weight of PVC.

UV absorbers and light stabilizers: examples of these are:

1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxy-phenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)-benzotriazole, 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxy-phenyl)benzotriazole, 2-(3',5'-bis(a,a-dimethylbenzyl)-2'-hydroxyphenyl)-benzotriazole, a mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzo-triazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chlorobenzo-triazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-

methylphenyl)benzotriazole, and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxy-carbonylethyl)phenylbenzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzo-triazol-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonyl-ethyl)-2'-hydroxyphenyl]benzotriazole with polyethylene glycol 300;

$$\left[RCH_2CH_2COO(CH_2)_3\right]_2$$

where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl.

2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivative.

3. Esters of substituted or unsubstituted benzoic acids, for example 4-tert-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxy-benzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

4. Acrylates, for example ethyl a-cyano-b,b-diphenylacrylate or isooctyl a-cyano-β,β-diphenylacrylate, methyl α-carbomethoxycinnamate, methyl a-cyano-b-methyl-p-methoxycinnamate or butyl α-cyano-β-methyl-p-methoxycinnamate, methyl a-carbo-methoxy-p-methoxycinnamate and N-(b-carbomethoxy-b-cyanovinyl)-2-methylindoline.

5. Nickel compounds, for example nickel complexes of 2,2'-thio-bis[4-(1,1,3,3-tetra-methylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of monoalkyl esters, such as of the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, such as of 2-hydroxy-4-methylphenyl undecyl ketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

6. Sterically hindered amines, for example bis(2,2,6,6-tetramethylpiperidyl) sebacate, bis(2,2,6,6-tetramethylpiperidyl) succinate, bis(1,2,2,6,6-pentamethylpiperidyl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) n-butyl 3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate,

tetrakis(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetraoate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl) malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-di(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione.

7. Oxalamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide and mixtures of o- and p-methoxy and of o- and p-ethoxy-disubstituted oxanilides.

8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis-(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropyloxy)-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropoxy)-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

The novel stabilizer mixture is preferred with alkali metal or alkaline earth metal carboxylates, especially calcium carboxylates, with aluminium carboxylates, with 1,3-dicarbonyl compounds, with dihydropyridines, with phosphites or with combinations of these substances.

Plasticizers: Examples of suitable organic plasticizers are those from the following groups:

A) Phthalic esters:
Examples of such plasticizers are dimethyl, diethyl, dibutyl, dihexyl, di-2-ethylhexyl, di-n-octyl, di-isooctyl, di-isononyl, di-isodecyl, di-isotridecyl, dicyclohexyl, di-methylcyclohexyl, dimethylglycol, dibutylglycol, benzyl butyl and diphenyl phthalate, and also mixtures of phthalates, such as C_{7-9}- and C_{9-11}alkyl phthalates from predominantly linear alcohols, C_{6-10}-n-alkyl phthalates and C_{8-10}-n-alkyl phthalates. Among these, preference is given to dibutyl, dihexyl, di-2-ethylhexyl, di-n-octyl, di-isooctyl, di-isononyl, di-isodecyl, di-isotridecyl and benzyl butyl phthalate and to the abovementioned mixtures of alkyl phthalates. Particular preference is given to di-2-ethylhexyl, di-isononyl and di-isodecyl phthalate, which are also known under the common abbreviations DOP (dioctyl phthalate, di-2-ethylhexyl phthalate), DINP (diisononyl phthalate), and DIDP (diisodecyl phthalate).

B) Esters of aliphatic dicarboxylic acids, especially esters of adipic, azelaic and sebacic acid
Examples of such plasticizers are di-2-ethylhexyl adipate, di-isooctyl adipate (mixture), di-isononyl adipate (mixture), di-isodecyl adipate (mixture), benzyl butyl adipate, benzyl octyl adipate, di-2-ethylhexyl azelate, di-2-ethylhexyl sebacate and di-isodecyl sebacate (mixture). Preference is given to di-2-ethylhexyl adipate and di-isooctyl adipate.

C) Trimellitic esters,
for example tri-2-ethylhexyl trimellitate, tri-isodecyl trimellitate (mixture), tri-isotridecyl trimellitate, tri-isooctyl trimellitate (mixture) and also tri-C_{6-8}alkyl, tri-C_{6-10}alkyl, tri-C_{7-9}alkyl and tri-C_{9-11}alkyl trimellitates. The latter trimellitates are formed by esterification of trimellitic acid with the corresponding mixtures of alkanols. Preferred trimellitates are tri-2-ethylhexyl trimellitate and the abovementioned trimellitates from alkanol mixtures. Common abbreviations are TOTM (trioctyl trimellitate, tri-2-ethylhexyl trimellitate), TIDTM (triisodecyl trimellitate) and TITDTM (triisotridecyl trimellitate).

D) Epoxy plasticizers
These are principally epoxidized unsaturated fatty acids such as epoxidized soybean oil.

E) Polymer plasticizers
The most common starting materials for the preparation of the polyester plasticizers are: dicarboxylic acids such as adipic, phthalic, azelaic and sebacic acid; and diols such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentylglycol and diethylene glycol.

F) Phosphoric esters
Examples of such phosphoric esters are tributyl phosphate, tri-2-ethylbutyl phosphate, tri-2-ethylhexyl phosphate, trichloroethyl phosphate, 2-ethylhexyl diphenyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and trixylenyl phosphate. Preference is given to tri-2-ethylhexyl phosphate and to ®Reofos 50 and 95 (from FMC).
G) Chlorinated hydrocarbons (paraffin)
H) Hydrocarbons
I) Monoesters, for example butyl oleate, phenoxyethyl oleate, tetrahydrofurfuryl oleate and alkylsulfonic esters.
J) Glycol esters, for example diglycol benzoates.

Definitions and examples of plasticizers from groups A) to J) can be found in the following handbooks:

"Taschenbuch der Kunststoffadditive", eds. R. Gächter and H. Müller, Carl Hanser Verlag, 1989, Chapter 5, pp. 341-442.

"PVC Technology", ed. W.V. Titow, 4th. Ed., Elsevier Publishers, 1984, Chapter 6, pages 147-180.

It is also possible to employ mixtures of different plasticizers.

The plasticizers can be employed in an amount of, for example, from 5 to 120 parts by weight, expediently from 10 to 100 parts by weight, based on 100 parts by weight of PVC.

Examples of suitable **lubricants** are: montan wax, fatty acid esters, PE waxes, amide waxes, chlorinated paraffins, glycerol esters or alkaline earth metals soaps, and silicone-based lubricants as described in EP 225261. Lubricants which can be used are also described in "Taschenbuch der Kunststoffadditive", eds. R. Gächter and H. Müller, Carl Hanser Verlag, 3rd edition, 1989, pages 478-488.

Fillers: Examples of possible fillers ("Handbook of PVC-Formulating" by E. J. Wickson, John Wiley & Sons, New York 1993, pp. 393-449) and reinforcing agents ("Taschenbuch der Kunststoffadditive", eds. R. Gächter and H. Müller, Carl Hanser Verlag, 3rd edition, 1989, pages 549-615) are: calcium carbonate, dolomite, wollastonite, magnesium oxide,

magnesium hydroxide, silicates, glass fibres, talc, kaolin, chalk, mica, metal oxides and metal hydroxides, carbon black or graphite), preference being given to chalk.

Pigments: Suitable substances are known to the skilled worker. Examples of inorganic pigments are TiO_2, carbon black, Fe_2O_3, Sb_2O_3, $(Ti,Ba,Sb)O_2$, Cr_2O_3, spinels such as cobalt blue and cobalt green, Cd(S,Se), ultramarine blue. Preference is given to TiO_2, including its micronized form. Examples of organic pigments are azo pigments, phthalocyanine pigments, quinacridone pigments, perylene pigments, pyrrolopyrrole pigments and anthraquinone pigments. Further details are to be found in "Handbook of PVC Formulating", E.J. Wickson, John Wiley & Sons, New York 1993, pp. 449 - 474.

Examples of the chlorine-containing polymers to be stabilized or their recyclates are: polymers of vinyl chloride, vinyl resins containing vinyl chloride units in their structure, such as copolymers of vinyl chloride and vinyl esters of aliphatic acids, especially vinyl acetate, copolymers of vinyl chloride with esters of acrylic and methacrylic acid and with acrylonitrile, copolymers of vinyl chloride with diene compounds and unsaturated dicarboxylic acids or their anhydrides, such as copolymers of vinyl chloride with diethyl maleate, diethyl fumarate or maleic anhydride, post-chlorinated polymers and copolymers of vinyl chloride, copolymers of vinyl chloride and vinylidene chloride with unsaturated aldehydes, ketones and others, such as acrolein, crotonaldehyde, vinyl methyl ketone, vinyl methyl ether, vinyl isobutyl ether and the like; polymers of vinylidene chloride and copolymers thereof with vinyl chloride and other polymerizable compounds; polymers of vinyl chloroacetate and dichlorodivinyl ether; chlorinated polymers of vinyl acetate, chlorinated polymeric esters of acrylic acid and of alpha-substituted acrylic acid; polymers of chlorinated styrenes, for example dichlorostyrene; chlorinated rubbers; chlorinated polymers of ethylene; polymers and post-chlorinated polymers of chlorobutadiene and copolymers thereof with vinyl chloride, chlorinated natural and synthetic rubbers; and mixtures of the abovementioned polymers with each other or with other polymerizable compounds.

In the context of this invention the term PVC also includes copolymers with polymerizable compounds such as acrylonitrile, vinyl acetate or ABS, which can be suspension, bulk or emulsion polymers. Preference is given to PVC homopolymer, alone or in combination with polyacrylates.

Also included are the graft polymers of PVC with EVA, ABS and MBS. Other preferred substrates are mixtures of the abovementioned homo- and copolymers, especially, vinyl

chloride homopolymers, with other thermoplastic and/or elastomeric polymers, especially blends with ABS, MBS, NBR, SAN, EVA, CPE, MBAS, PMA, PMMA, EPDM and polylactones.

Preference is given to suspension polymers and bulk polymers, and to emulsion polymers.

A particularly preferred chlorine-containing polymer is polyvinyl chloride, especially as suspension polymer and bulk polymer.

For stabilization in the context of this invention, further suitable polymers are, in particular, recyclates of chlorine-containing polymers, these polymers being the polymers described in more detail above that have undergone damage through processing, use or storage. PVC recyclate is particularly preferred. The recyclates may also include small amounts of extraneous substances, for example paper, pigments, adhesives, which are often difficult to remove. These extraneous substances may also arise from contact with various materials in the course of use or of reprocessing, examples being residues of fuel, fractions of coating material, traces of metal and residues of initiator.

The stabilizer mixture is employed in a manner familiar to the skilled worker.

It is also possible, for instance, for the stabilizer mixture to be processed together with conventional additives, prior to the actual use, by shaping it into, for example, granules or extrudate or a paste.

The present invention additionally provides for the use of the above-described stabilizer mixture - as granules, extrudate or paste and/or in conjunction with lubricants (so-called *one-pack* formulations) - for stabilizing a halogen-containing polymer or polymer recyclate. For the individual stabilizers and for the halogen-containing polymer itself, the preferences expressed above apply; similarly, one of the above-described additional constituents can be employed.

The stabilizer mixture can be added to the polymer in a known manner, the abovementioned stabilizers and, if desired, further additives being mixed with the halogen-containing polymer using known devices such as mixers, compounders, extruders, mills and the like. In this context the stabilizers can be added individually or as a mixture or else in the form of so-called masterbatches. The invention consequently also provides a process for stabilizing halogen-containing polymer, which comprises mixing the stabilizer components and, if desired, further additives with the PVC using devices such as calenders, mixers, compounders, extruders and the like.

The invention also relates to the polymer compositions stabilized in this way comprising the novel stabilizer mixture. They can be brought into the desired form by known methods. Examples of such methods are calendering, extrusion, injection moulding, sintering or spinning, and also extrusion blow moulding or processing by the plastisol process. The polymer compositions can also be processed to foams.

The invention also relates to the use of the stabilized polymer compositions for preparing mouldings which can be prepared from halogen-containing polymer. The novel polymer compositions are suitable for semirigid and flexible formulations, for example for flexible formulations for wire sheathing and cable insulation. In the form of semirigid formulations, the novel polymer compositions are suitable for decorative films, foams, agricultural films, hoses, sealing profiles, office films, extruded profiles and sheets, flooring films and sheets, coated products and synthetic leathers, and also crashpad sheets (for use in the automotive sector).

In the form of rigid formulations, the novel polymer compositions are suitable for hollow articles (bottles), packaging films (thermoform films), blown films, crashpad sheets (cars), pipes, foams, heavy profiles (window frames), transparent wall profiles, construction profiles, sidings, fittings and apparatus enclosures (computers, domestic appliances) and also other injection-moulded articles.

Examples of the use of the polymer compositions stabilized in accordance with the invention as plastisol are artificial leathers, flooring, textile coatings, wallpapers, coil coatings and underbody protection for motor vehicles.

Examples of sinter applications of the polymer compositions stabilized in accordance with the invention are slush, slush mould and coil coatings.

The **preparation** of the N-piperidinyltriazines is known from the literature (cf. e.g. Houben-Weyl "Methoden der organischen Chemie" Vol. VIII, pp. 233-237, SAUERSTOFFVERBINDUNGEN III, 3rd Ed., Thieme Verlag Stuttgart 1952). As starting material for the reaction with various N-piperidinylamines it is possible to employ cyanuric chloride, diamino-chloro-1,3,5-triazine or variously substituted bisdialkylamino-chloro-1,3,5-triazines or dialkylamino- and/or alkylamino-dichloro-1,3,5-triazines.

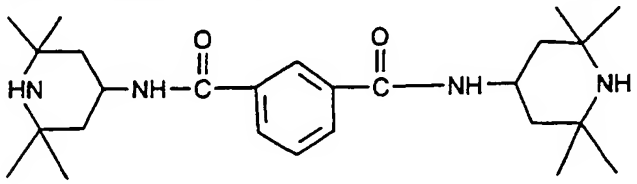
The **examples** which follow illustrate the invention in more detail without restricting it. As in the remainder of the description, parts and percentages are by weight unless stated otherwise.

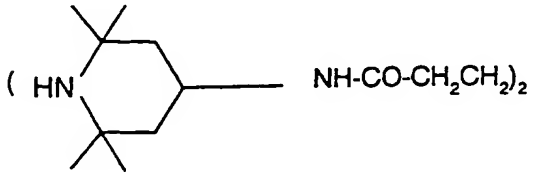
Example 1: N,N'-bis[2,2,6,6-tetramethylpiperidin-4-yl]oxamide

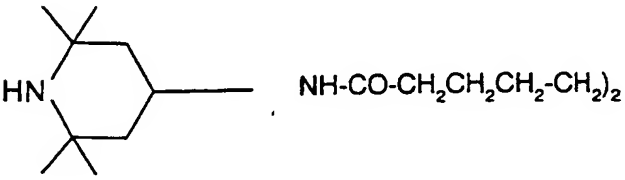
156.3 g (0.8 mol) of 4-amino-2,2,6,6-tetramethylpiperidine are added slowly with stirring to 56.1 g (0.4 mol) of diethyl oxalate, aminolysis taking place with severe evolution of heat. The temperature rises to about 100°C. Following the addition of 150 ml of xylene, ethanol is distilled off at 88-137°C over the course of 18.5 hours. The batch is subsequently taken up in 1500 ml of xylene, filtered while hot, and cooled. The precipitated crystals are filtered off with suction and recrystallized from xylene.

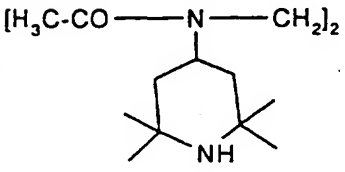
Yield 120g (82% of theory) m.p. 225-231°C.

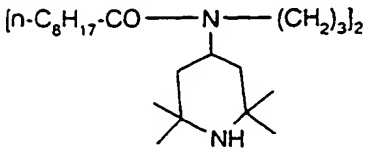
The following products (Examples 2 - 8) were prepared by reacting 4-amino-2,2,6,6-tetramethylpiperidine with the corresponding acid chlorides or by reacting bis-2,2,6,6-tetramethylpiperidinyl-1,6-hexanediamine with acetic anhydride:

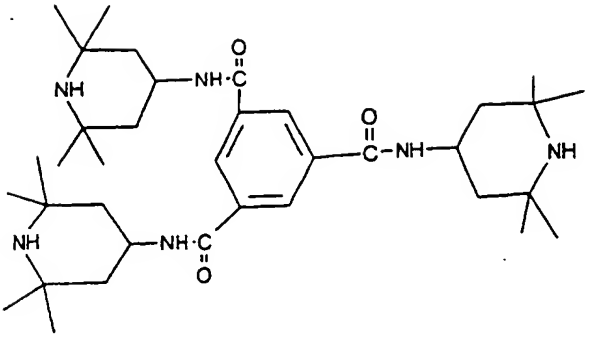
2:  m.p. 273°C decomp.;

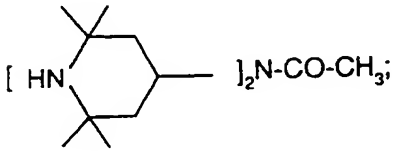
3:  m.p. 217°C;

4:  m.p. 145°C;

5:  m.p. 197-199°C;

6:  m.p. 79-81°C;

7:  m.p. > 300°C ;

8:  m.p. 140-143°C.

Example **9:** For preparing the stabilizers I and II, a Zn/Ca stearate mixture is mixed intensively with a commercial beta-diketone (stab. I) and also with the piperidine compound **5** in a ratio of 8:2:1.5 (stab. II) in a tumble mixer for a period of 1.5 hours. Of these stabilizer mixtures, portions of 1.0 part (stab. I) or 1.15 parts (stab. II) are each mixed with 100 parts of S-PVC (K value 70) and 21 parts of a mixture of dioctyl phthalate/epoxidized soya oil and with a commercial liquid aryl-alkyl phosphite, and the mixture is plasticated on mixing rollers at 190°C for 5 minutes. Test specimens are cut from the resulting sheets (thickness 0.2 mm) and are subjected to thermal stress in a Mathis Thermotakter at 180°C for the period indicated in Table 1 below. Subsequently the Yellowness Index (YI) is determined in accordance with ASTM-1925-70.

The lower the YI value found, the more effective the prevention by the stabilizer system of yellowing and therefore of damage to the material. The long-term thermal stability of the stabilized polymer is evident from the sudden onset of massive discolouration. A stabilizer is all the more effective the longer this discolouration is delayed under thermal stress conditions.

Heat test: YI of test specimens at 180°C

Table 1

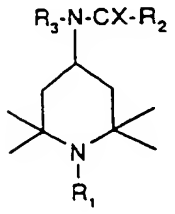
Stabilizer	*Coadditive*	*Test duration [min]*					*Interrupted at time [min]*
		0	*6*	*12*	*24*	*48*	
I	-	5.1	5.4	5.3	black	black	17
II	Compd. 5	5.7	6.0	6.5	7.9	12.8	70

WHAT IS CLAIMED IS:

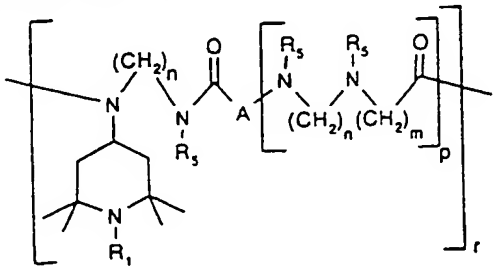
1. A stabilizer combination for halogen-containing polymers, comprising

A) at least one organozinc compound with a Zn-O bond and/or a Zn-S bond

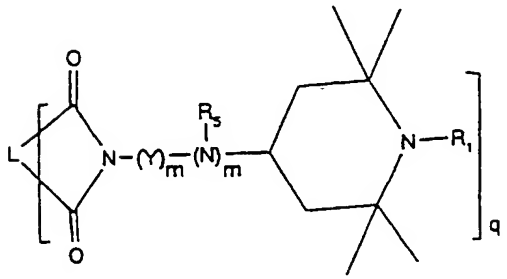
B) at least one compound of the formula



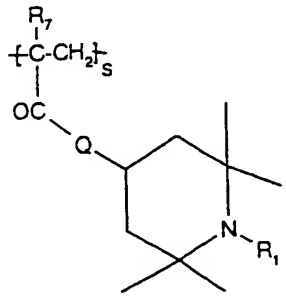
(I),



(II),



(III) and/or



(IV),

in which the radicals and symbols have the following meanings:

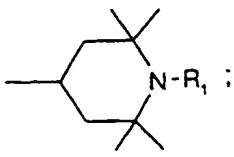
X: O or S;

a: 0 to 8; b: 2 to 12; c: 1 or 2; k: 2 to 6;

R_1 : H or C_1-C_8alkyl, C_3-C_8alkenyl, C_7-C_9phenylalkyl or C_5-C_8cycloalkyl;

R_2 : C_1-C_8alkyl, -NH_2, R_3NG-, R_4-O-, $[R_3$-NG-CX$]_c$E-,

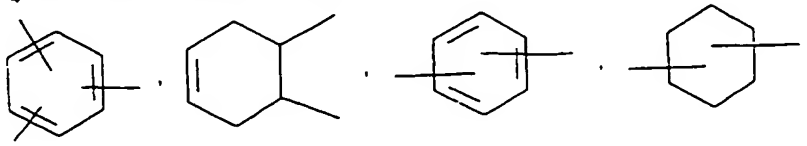
$(C_1$-C_4alkyl$)_2N(CH_2)_k$-CX-, phenyl or OH-, C_1-C_4alkoxy- or C_1-C_4alkyl-substituted phenyl,

G:  ;

R_3: H, C_1-C_8alkyl, C_3-C_8alkenyl, C_5-C_8cycloalkyl, R_2-CX-NG-$(CH_2)_b$,

$(C_1$-C_4alkyl$)_2N(CH_2)_k$- or G;

R_4 : C_1-C_4alkyl, cyclohexyl or benzyl;

E: $(CH_2)_a$,  .

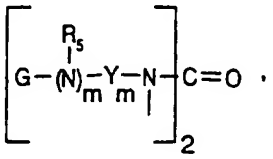
-CH=CH-, -CH(OH)-CH(OH)-, $-CH_2$-CH(OH)- or -NH $(CH_2)_b$NH-;

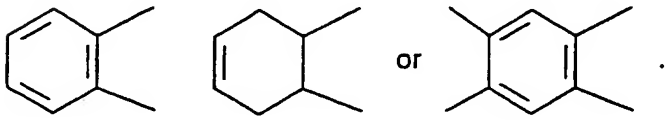
A: >CO, $-(CH_2)_m$-, $-(CH_2)_d$-CO- or -NH$(CH_2)_n$-CO-

m: 0 or 1; n: 2 to 12; p: 0 or 1; d: 1 to 8; q: 1 or 2; r: 2 to 50;

and, if p is 0, A: >CO, $-(CH_2)-_m$, $-(CH_2)_d$-CO-, -NH$(CH_2)_n$-CO-

if p is 1, A: $(CH_2)_m$;

the group L: $-CH_2-CHR_6-$, $-(CH_2)_3-$, -CH=CH-, 



R_5 : H, C_1-C_8alkyl, C_3-C_8alkenyl, C_5-C_8-cycloalkyl or G;

R_6 :H, C_1-C_{12}alkyl;

R_7 : H or CH_3;

Q: -O- or >NH;

Y : $-CH_2$-CH(OH)-CH_2-;

and s: 3 to 60.

2. A stabilizer combination according to claim 1, in which the radicals and symbols have the following meanings:

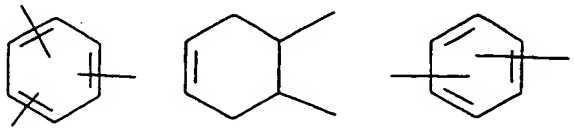
X: O or S;

a: 0 to 4; b: 2 to 6; c: 1 or 2; k: 2 or 3;

R^1 : H or C_1-C_8alkyl;

R_2 : C_1-C_8alkyl, $-NH_2$, R_3-NG-, $[R_3$-NG-CX$]_c$E- or $(C_1$-C_4alkyl$)_2N(CH_2)_k$-CX-;

R_3 : H, C_1-C_8alkyl, R_2-CX-NG-$(CH_2)_b$, $(C_1$-C_4alkyl$)_2N(CH_2)_k$- or -G;

E: $-(CH_2)_a$-,  -CH=CH- or

-NH $(CH_2)_b$NH-;

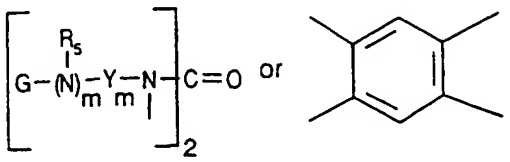
R_5 : H, C_1-C_8alkyl or G;

A: -CO-, -$(CH_2)_m$- , -$(CH_2)_d$-CO- or -NH$(CH_2)_n$-CO-;

m: 0 or 1; n: 2 to 6; p: 0 or 1; d: 1 to 4; q: 1 or 2; r: 2 to 50;

and, if p is 0, A: -CO-, -$(CH_2)_m$- , -$(CH_2)_d$-CO- or -NH$(CH_2)_n$-CO-;

if p is 1, A: -$(CH_2)_m$- ;

the group L: -CH_2-CHR_6-, -$(CH_2)_3$-,  or ;

R_6 : H or C_1-C_{12}alkyl;

Y: -CH_2-CH(OH)-CH_2- ;

R_7 : H or CH_3;

Q: -O- or >NH, and s: 3 to 60.

3. A stabilizer combination according to claim 1, in which the radicals and symbols have the following meanings:

X: O;

a: 0 to 4; b: 2 to 6; c: 1;

R_1 : H or C_1-C_8alkyl;

R_2 : $[R_3$-NG-CX$]_c$E-;

R_3: H, C_1-C_8alkyl, R_2-CX-NG-$(CH_2)_b$ or G;

E: $(CH_2)_a$ or -NH-$(CH_2)_b$NH-;

R_5 : G;

A : -$(CH_2)_m$- ;

m: 0 or 1; n: 2 to 6; p: 0 ; q: 1 or 2; r: 2 to 50;

the group L: -CH_2-CHR_6-, -$(CH_2)_3$-, or -CH=CH-;

R_6 : H;

Y : -CH_2-CH(OH)-CH_2- ;

R_7 : H ;

Q: >NH; and s: 3 to 60.

4. A stabiliser combination according to claim 1 in which the organozinc compound has a Zn-O bond.

5. A stabiliser combination according to claim 1 in which the organozinc compound is a zinc carboxylate.

6. A stabiliser combination according to any preceding claim which additionally comprises alkali metal compounds and/or alkaline earth metal compounds and/or aluminium compounds.

7. A stabiliser combination according to any preceding claim which additionally comprises calcium carboxylates.

8. A stabiliser combination according to any preceding claim which additionally comprises aluminium carboxylates.

9. A stabiliser combination according to any preceding claim which additionally comprises at least on further substance from the group consisting of the epoxides and epoxidised fatty acid esters, phosphites, thiophosphites and thiophosphates, polyols, 1,3-carbonyl compounds, mercaptocarboxylic esters, dihydropyridines, antioxidants, light stabilisers and UV absorbers, alkali metal compounds and alkaline earth metal compounds, perchlorate salts, zeolites, hydrotalcites and dawsonites.

10. A stabiliser combination according to any one of the preceding claims in which at least some of the organozinc compound is replaced by an inorganic zinc compound.

11. A composition comprising a halogen-containing polymer and a stabiliser combination according to any one of the preceding claims.

12. A process for stabilising halogen-containing polymers, which comprises adding to them a stabiliser combination according to any one of claims 1 to 10.

13. A stabiliser combination according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing Examples.

The Patent Office

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Application No:	GB 9705846.5	**Examiner:**	Miss Maureen M. Kelman
Claims searched:	1 to 13, in respect of a combination containing compound (I)	**Date of search:**	26 June 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3K KCZ

Int Cl (Ed.6): C08K 5/00, 5/138, 5/3435, 5/36

Other: ONLINE: CHABS, CLAIMS, JAPIO, RAPRA, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	EP 0446171 A2	CIBA-GEIGY	
A	EP 0421933 A1	CIBA-GEIGY	
X	US 5350785 A	CIBA-GEIGY see the claims, formula (V) in column 9 and column 34, line 43, to column 35, line 3	1-7, 9-13
X	US 5283273 A	CIBA-GEIGY see the claims and formula (III) in column 4	1-7, 9-13
X	US 5244949 A	CIBA-GEIGY see the claims and formula (III) in column 4	1-6, 9-13

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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